The Multishell EXAFS Fit Program

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I. Program purpose and formalism

This program fits EXAFS filtered or unfiltered data to a shell model based on model or calculated amplitudes and phases. The idea is that the unknown spectrum is modeled as a sum of shells which are like those in some reference, but with different coordination numbers, distances, energy references and Debye-Waller parameters. The EXAFS from one of the references is considered to be given by a general plane-wave formula:

$$\chi_i(k) = A_i(k)\sin(2kR_i + \phi_i(k)) = A_i(k)\,\mathrm{Im}\left[\exp(i(2kR_i + \phi_i(k))\right] \tag{1}$$

The amplitude term $A_i(k)$ includes the inverse-square, Debye-Waller, S_0^2 and inelastic-scatter effects. The phase term $\phi_i(k)$ includes curved-wave effects. Therefore, if the distance for the reference isn't too different from that in the unknown, the curved-wave effects cancel out.

Now, we consider the EXAFS from the unknown to be a sum of terms like (1). We allow there to be a shift in distance, a difference in ratio, a small shift in the energy origin (ΔE_0) and a difference in Debye-Waller factor (mean-square relative displacement, $\Delta\sigma_i^2$). In addition, we allow the distribution of distances to be asymmetrical. The assumption is that the distribution is given by a Gaussian convolved with an exponential tail:

$$\rho(r) \propto \exp\left(-\frac{(r-r_0)^2}{2\sigma^2}\right) \otimes T(r) \tag{2}$$

where $\otimes$ represents convolution and the exponential tail function is:

$$T(r) = \begin{cases} \exp(-(r-r_0)/w) & (r-r_0)w \geq 0 \\ 0 & (r-r_0)w < 0 \end{cases} \tag{3}$$

If $w = 0$, you get the traditional Gaussian function typically assumed. Otherwise, the distribution has a tail which extends to the right ($w > 0$) or the left ($w < 0$). This

asymmetry is used to model such effects as anharmonicity. This form has the advantage that while the distribution function is complicated in real space, it's simple in *k*-space. The Fourier transform of (2) is

$$\tilde{\rho}(k) \propto \frac{\exp(2ik(r - r_0 - w) - 2k^2\sigma^2)}{1 - 2ikw}. \tag{4}$$

I prefer this form to a cumulant expansion because the latter doesn't always converge, and this form yields a physically plausible form for the distribution in real space. The form (2) is essentially a simple model which yields all the cumulants.

Putting it all together, what the fit program fits to is this:

$$\chi(k) = \sum_{shell\ i} b_i A_i(k) e^{-2k^2\Delta\sigma_i^2} \operatorname{Im}\left(\frac{\exp(i\theta_i)}{1 - 2ikw_i}\right) \tag{5}$$

where the phase is given by

$$\theta_i = \phi_i(k) + 2k(r - w_i - R_i) + \Delta E_0 K^2 (r - w_i)/k \tag{6}$$

The symbols just introduced are:

b_i The relative amplitude (coordination number, corrected for inverse-square and exponential-loss terms) for the shell *i*. For example, if the reference has 6 neighbors at a distance of 2 Å and the unknown has 12 at a distance of 2.5 Å, then $b_i = \frac{12}{6}\left(\frac{2}{2.5}\right)^2 = 1.28$, not counting the contribution from the inelastic-loss term.

R_i The distance in reference shell *i*.

$\Delta\sigma_i^2$ The difference in mean-square relative displacement between the unknown and the reference. A positive number here means that the distribution in the unknown is wider than in the reference.

ΔE_0 The difference in energy origin between the unknown and reference. The form used is an approximation good when ΔE_0 is small (<10eV).

w_i The asymmetry parameter for the i^{th} shell.

K The energy-wavevector conversion coefficient, about $0.5132\ \text{Å}^{-1}\text{eV}^{-1/2}$.

This long mathematical diversion was intended to make it clear just what the program fits so that the parameters make sense.

Like any non-linear least-squares fitting problem, EXAFS fitting often has multiple optima in parameter space. Therefore, one needs to be able to specify starting values for parameters and allow only selected ones to float. Selective freeing of parameters is also key to one method of error estimation. In this method, one frees all relevant parameters except one, then repeats the fit for various values of the fixed parameter, seeing how the sum-squared residual varies. By allowing the other parameters to float, you automatically take parameter correlations into account. Thus, if you fix the coordination number and make it go up, the mean-square relative displacement also goes up in order to make the amplitude stay roughly the same in the middle of the data range.

II. Initialization

The program operates in two stages. In the first, you specify the file to be fitted and those to be used as references. You also specify the distances for the references. The second stage is the actual fitting routine, in which you can explore parameter space.

In order to explain how the program works, we will go through a demonstration example. In this example, the unknown is Cr foil. Cr is a BCC crystal and has a split first shell with 8 neighbors at 2.491 Å and 6 at 2.885 Å. We'll pretend we don't know this, but know only that Cr has a split first shell. For a reference, we'll use Cu foil, in which the first shell contains 12 neighbors at 2.556 Å. We'll pretend that the scattering amplitude and phase from Cu looking at Cu (Z=29) is the same as from Cr (Z=24) looking at Cr. As we'll see, we won't quite get the right answer for coordination number or distance because of this error. Were we doing this 'for real', we'd 'correct' the amplitudes and phases of Cu using FEFF calculations so as to better represent Cr.

When you start the program, it asks first for a file to fit, then for amplitude and phase files for the references. These amplitude and phase files are what come out of the FT program, and are tables of $A(k)$ vs. k and $\phi(k)+2kR$ vs. k, so the filtered reference file `ref.f` may be reconstructed as `ref.a`*sin(`ref.p`). It keeps asking for amplitude and phase files until you hit the `Cancel` button in the file dialog. That's how it knows how many references to use. In our case, we will use the filtered first-shell files `cufoil.a` and `cufoil.p` for both shells. Once you have hit the Cancel button, the

screen looks like that shown in Figure 1. After entering the filenames, you have to fill in the reference distances in the list on the right side of the screen. The program will automatically display as many spaces for distances as there are shells (amp&phase pairs). Only after at least one pair of amplitude and phase has been entered, and after all the distances have been filled in, will the Enter Fit Screen button be enabled. Pushing this button gets you to the fit program proper.

III. Fitting

The fit screen starts out looking as shown in Figure 2. To the left are displayed the fit parameters and their float/fix status. The green buttons below each number are dark if the parameter is considered fixed and turn bright when it floats. There are two columns of fit parameters, corresponding to the two shells specified in the initial screen. The parameters are set to a default, which describes the unknown as being identical in every way to the first shell, with a zero contribution from the second. The shell distances are set to the ones specified for the reference. Above the list of parameters is a control labeled Amp Mode. It has two settings. In the default setting shown here, the first number for the amplitudes (second row of the parameter list) is the total relative coordination number $\sum_i b_i$ and the second (and all others, for >2 shells) is the fractional contribution from each shell, $b_i / \sum b_i, i > 1$. The name associated with these numbers is displayed as Total&fraction, to remind us of the mode. If we were to move the Amp Mode switch to the other setting, Separate Amps, the parameters would be simply the separate b_i, and the name would change to Relative CNs (coordination numbers). For example, using the same logic as on Page 2, we can compute the expected b_i for the Cr shells as being 0.652 and 0.380, assuming a 10 Å inelastic loss length (not a big effect). Thus, in Total&fraction mode, the first number would be 0.652+0.380=1.032 and the second 0.380/1.032=0.368. In Separate Amps mode, the numbers would be entered as 0.652 and 0.380.

The $\Delta\sigma_i^2$ are referred to on the screen as DWFs (Debye-Waller factors), even though that name properly refers to $\exp(-2k^2\Delta\sigma_i^2)$ instead. The units are 10^{-4} Å^2. The energy shifts are in units of eV.

To proceed with the fit, you enter your guesses for the parameters into the appropriate controls in the parameter list, push the Float buttons as desired, then hit Start Fit. For this fit, I started by floating only the distances and amplitudes, got a reasonable fit, then floated the DWFs as seen in Figure 3. When you hit Start Fit, the Working... light comes on and the Iteration Count indicator spins up. The parameters change before your eyes. If you see it going off into the weeds, say with huge values of the DWFs or energy shifts, you can hit the Stop fit button. In this case, we see that the fraction of second shell is about as predicted (0.33 vs. 0.38), but the total coordination is out, probably because of the difference between the scattering amplitude from Cu and Cr. Similarly, while the first-shell distance is out by 0.073 Å, their difference, 0.367 Å, is out by only 0.02 Å.

The Slave E0 switch is used to make the energy shifts of all shells stay equal during the fit. This is used, for instance, when the only degree of freedom in that regard is the energy shift of the unknown itself.

The fit can be saved in a 2-column file with default extension `fit`. This is useful for a variety of purposes, including subtracting a fit from an unfiltered file (using `plot-add-multiply`) and then submitting the result to the FT program, in order to pull out a weak shell from under a strong one.

The fit parameters can be saved in a file which looks like this:

```
[All shells]
# of shells=2
Amp mode=0
Slave E0?=FALSE
[Shell 0]
Model distance=2.556000
Distance=2.424656
Rel. CN=2.651204
Asym=0.000000
DWF=0.006159
DeltaE0=0.000000
[Shell 1]
```

```
Model distance=2.556000
Distance=2.791530
Rel. CN=0.326464
Asym=0.000000
DWF=0.000302
DeltaE0=0.000000
```

This is a config-type file with sections for each shell and one which pertains to all shells.

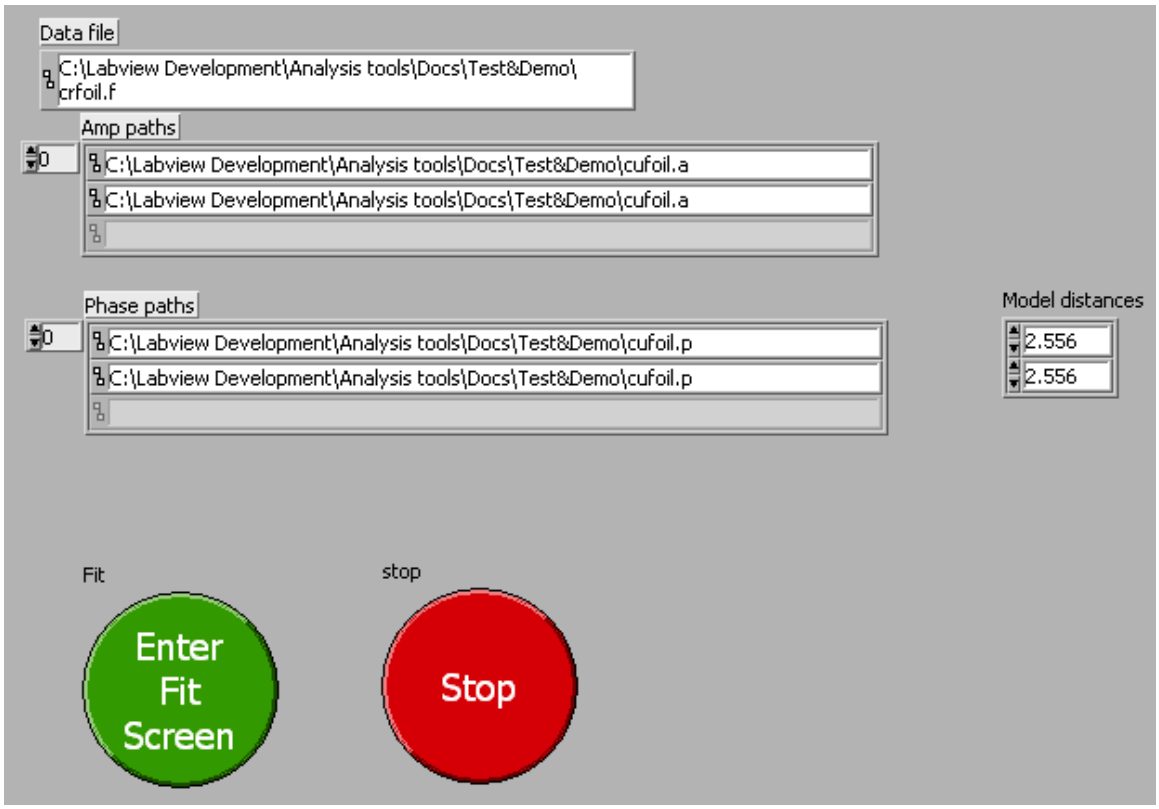

Figure 1. The starting screen, after files and distances have been entered. Because at least one amplitude and phase file, plus as many distances as there are shells have been entered, the Enter Fit Screen *button is enabled, allowing us to proceed.*

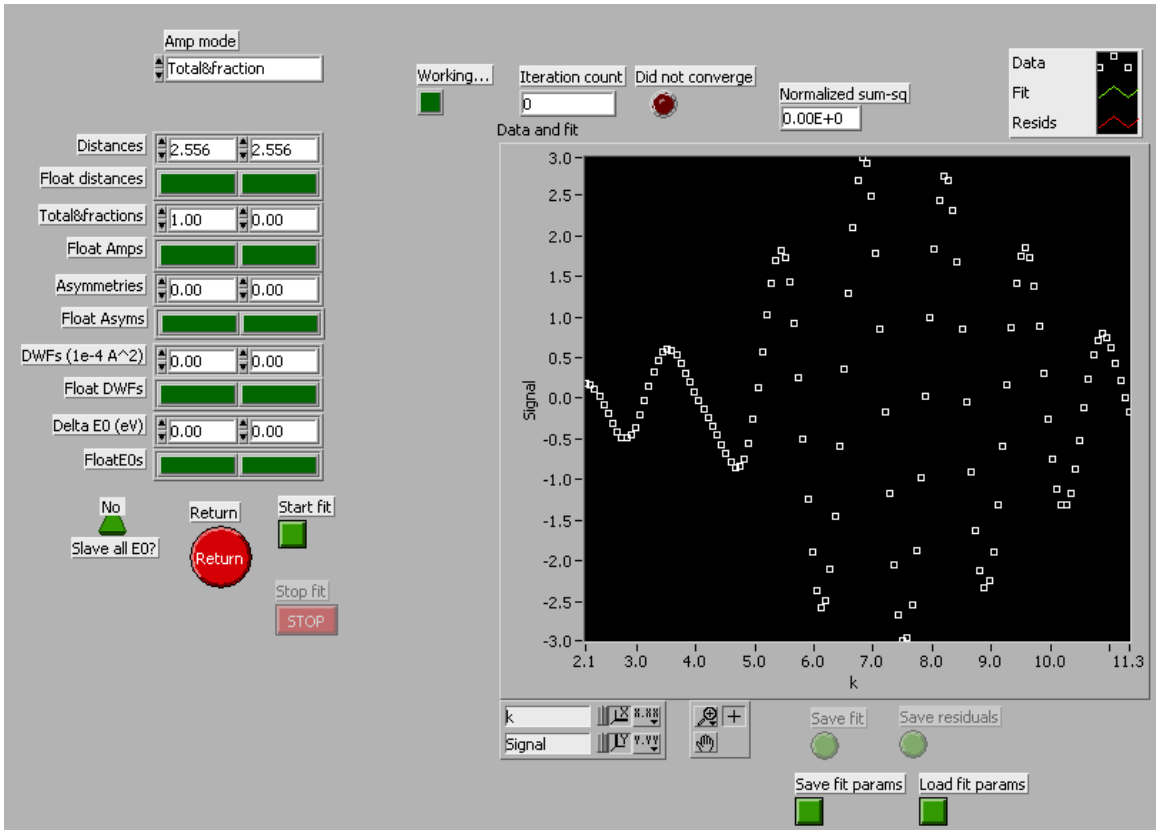

Figure 2. The initial state of the fit screen, after the Enter Fit Screen *button shown in Figure 1 is pressed. There are two columns of fit parameters because there are two shells.*

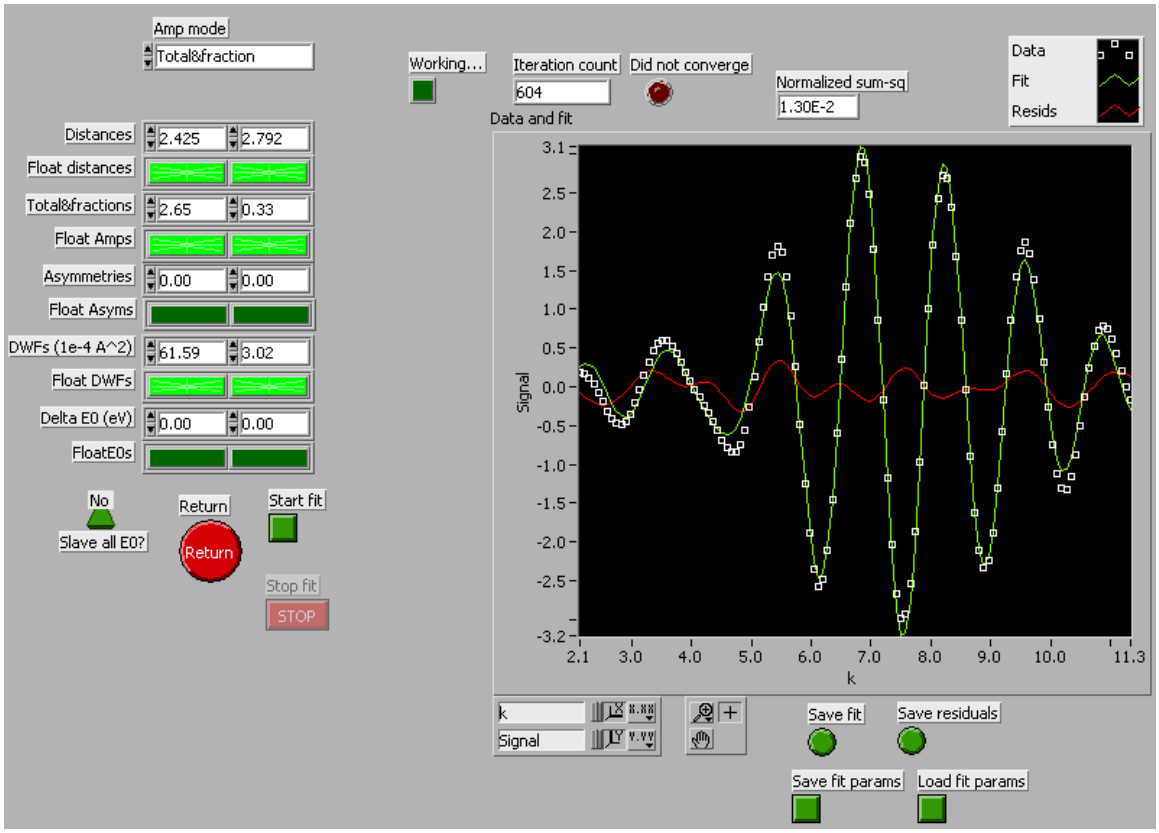

Figure 3. Fit screen after floating some parameters and hitting Start Fit. *The distances, amplitudes and DWFs are floated; the rest of the parameters are fixed.*